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PLUTONIUM SCRAP PROCESSING AT THE LOS ALAMOS  
SCIENTIFIC LABORATORY

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# LOS ALAMOS SCIENTIFIC LABORATORY

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## PLUTONIUM SCRAP PROCESSING AT THE LOS ALAMOS

### SCIENTIFIC LABORATORY

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#### ABSTRACT

The Los Alamos Scientific Laboratory currently has the newest plutonium handling facility in the nation. Los Alamos has been active in the processing of plutonium almost since the discovery of this man-made element in 1941. One of the functions of the new facility is the processing of plutonium scrap generated at LASL and other sites. The feed for the scrap processing program is extremely varied, and a wide variety of contaminants are often encountered. Depending upon the scrap matrix and contaminants present, the majority of material receives a nitric acid/hydrofluoric acid or nitric acid/calcium fluoride leach. The plutonium nitrate solutions are then loaded onto an anion exchange column charged with DOWEX 1 x 4, 50 - 100 mesh, nitrate form resin. The column is eluted with 0.48 M hydroxyl amine nitrate. The  $\text{Pu}(\text{NO}_3)_3$  is then precipitated as plutonium III oxalate which is calcined at 450 - 500°C to yield a purified  $\text{PuO}_2$  product.

#### INTRODUCTION

The Los Alamos Scientific Laboratory has one of the newest plutonium handling facilities in the nation (Figure 1, CN79-6775). The facility began operation in 1978 and consists of four areas:

100 Area	Advanced Fuels Research and Development
200 Area	Pu-238 Extraterrestrial Heat Source Program and Special Isotope Program
300 Area	Weapons Research and Development
400 Area	Chemical Operations



FIGURE 1 TA-55 Plutonium Handling Facility

The Chemical Operations Section is composed of the following programs:

Fast Flux Test Facility Plutonium Oxide Production

Americium Oxide Production

Plutonium Metal Production

Plutonium Scrap Recovery Programs

The plutonium scrap recovery program is responsible for the processing of Pu contaminated scrap from production programs and research and development work at Los Alamos and other sites across the nation.

The Chemical Operations portion of the plutonium handling facility contains one of the most versatile Pu scrap processing programs due to the unique equipment design and process philosophy. This allows for the head-end portion of the process to receive a wide range of scrap matrices and contaminants. Figure 2 (CN79-575) illustrates the typical glovebox design used in the scrap processing operations.

#### CHEMICAL PROCESSING

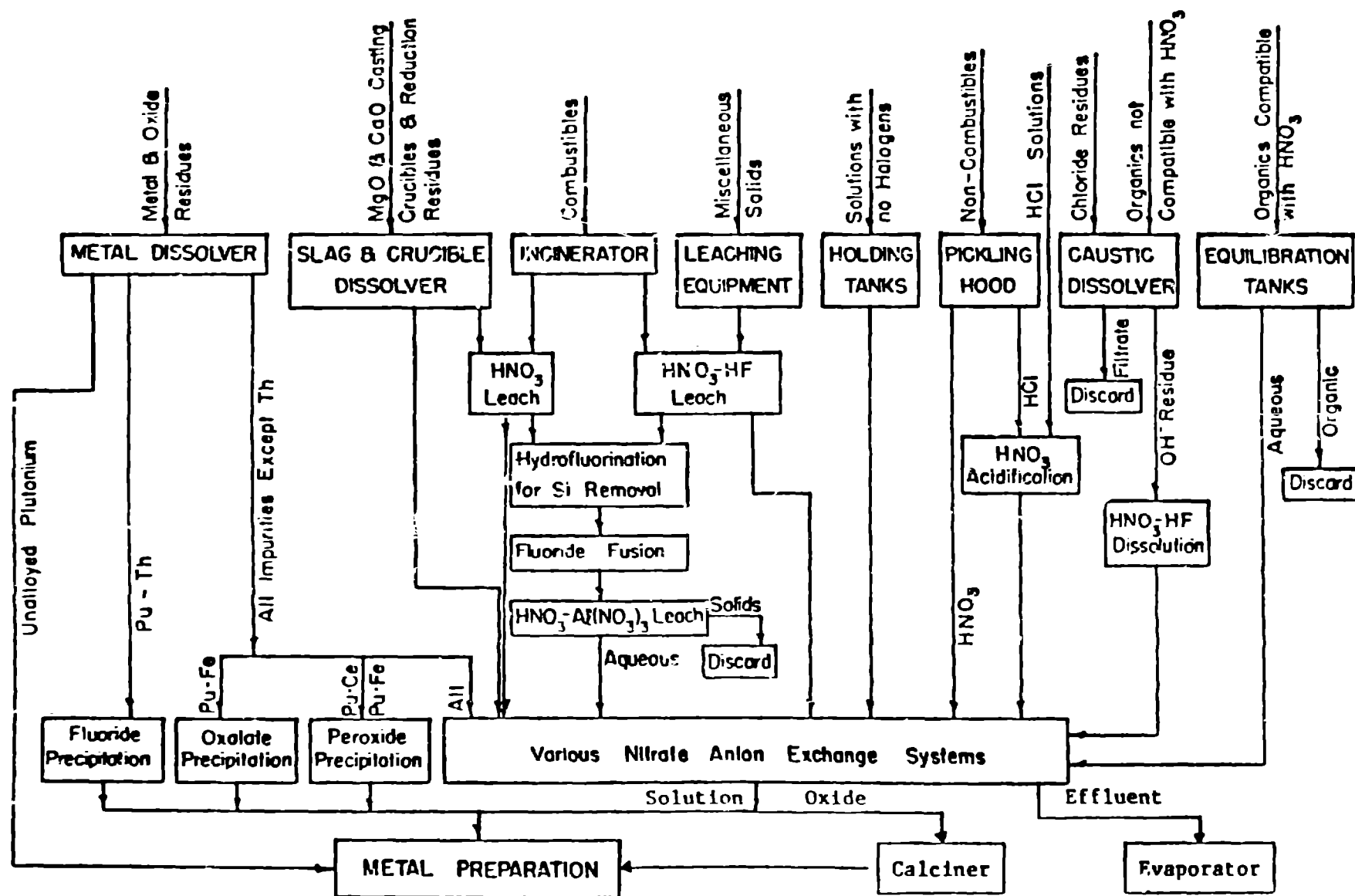
Figure 3 shows the overall flow of material in the scrap processing program. The general goal is to process the scrap material to a point where the plutonium is in solution as plutonium nitrate, and the remaining scrap residue contains residual plutonium contamination low enough to meet the Department of Energy (DOE) approved discard limits.

Prior to actual processing, the contaminated material is measured using nondestructive assay (NDA) techniques to determine the amount of plutonium present. Material that contains plutonium below a certain approved discard value is packed for shipment to 20-year retrievable storage. The material having plutonium contamination that is economically recoverable is then introduced into the process stream at a point compatible with the scrap matrix and contaminants present.



FIGURE 2 Typical Glovebox Design

FIGURE 3 Flow of Material in Chemical Operations Scrap Recovery



At Los Alamos, contaminated residues are initially divided into two main classes:

1. combustible items which are suitable feed for the incinerator
2. non-combustible items that will require chemical processing.

Incineration of combustible residues serves to reduce the volume of materials to be handled and produces ashes that can be processed as an impure  $\text{PuO}_2$ . Items such as rubber gloves and plastic which are usually classed as combustible are not considered to be suitable feed at LASL for the incinerator due to the rapid buildup of tars and residues in the scrubber and off-gas lines when items of this type are burned. The corrosion of the incinerator is increased notably when polyvinyl chloride plastics are burned thus releasing chlorine which forms hydrochloric acid when contacted with water. Figure 4 shows the flow diagram for the operation of the incinerator.

The ashes are collected after each run and ground by rod milling so that the resulting particles will pass through a 20 mesh screen. The ashes are then canned in 600 g lots to await chemical processing.

The second main class of residues, non-combustible scrap, can be divided into two groups:

1. items that can be decontaminated by an acid leach of the surface
2. items that require an acid dissolution of plutonium salts such as  $\text{PuO}_2$ .

Surface contaminated items such as plastic, plastic bags, and rubber glovebox gloves can often be decontaminated by wiping the item with a cloth wetted with dilute  $\text{HNO}_3$ . This procedure is most effective on items recently removed from service. The longer the plutonium is in contact with the rubber or plastic, the more imbedded the contamination becomes and the more rigorous the process is that must be employed to remove the Pu. Items with

Rags, Paper, and Similar Combustibles  
Normally Dried Before Loading

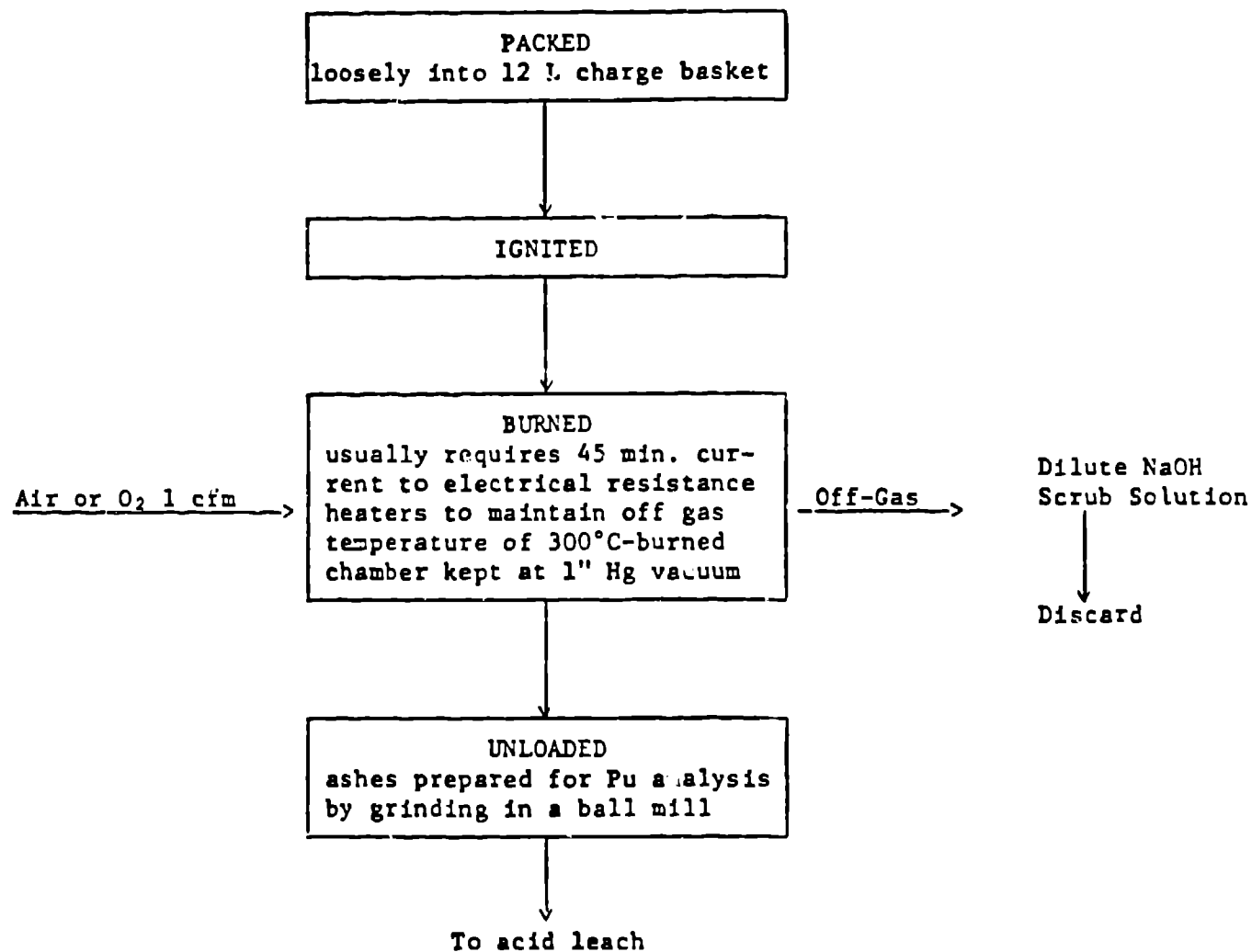


FIGURE 4 Operation of Process Residue Incinerator



imbedded contamination are cut into strips and heated in refluxing 10 M  $\text{HNO}_3$  - 0.1 M  $\text{HF}$  for 2 - 4 hours. The residues are then filtered, washed with dilute  $\text{HNO}_3$ , dried, and assayed using an in-line thermal neutron counter to determine the remaining plutonium level. A Pu content greater than the discard limit requires a second leach or incineration. If the Pu content is below the discard limit, then the item can be sent to retrievable storage.

Surface contaminated items such as tantalum molds and crucibles, sintered glass frits,  $\text{Al}_2\text{O}_3$  crucibles, and stainless steel filters are routinely decontaminated by leaching with a solution of 10 M  $\text{HNO}_3$  - 0.05 M  $\text{HF}$  for 2 - 4 hours under reflux conditions.

Contaminated heating mantles and absolute filters are disassembled, the contaminated portions placed in a 5 liter dissolving pot (Figure 5), and leached with a solution of two liters of 10 M  $\text{HNO}_3$  and 47 grams of  $\text{CaF}_2$  for 3 - 4 hours under reflux conditions. The solution is then cooled, filtered, and the filter residue washed with dilute acid and dried. The dried residue is then discarded or recycled depending upon the plutonium content.

Ashes from the incineration of rags, paper, wood, and other combustibles have plutonium levels ranging from 0.2 to 57% by weight. The ashes are leached according to the flow diagram in Figure 6 in the standard 5 liter dissolving pot fitted with a water jacketed reflux condenser or in a 6 inch diameter by 3 foot long glass tank fitted with steam coils. The ashes may be dissolved by repeated refluxing in  $\text{HNO}_3$  -  $\text{HF}$ . Studies have shown that the dissolution rate is directly proportional to the fluoride ion concentration up to 0.4 M, indicating that higher fluoride concentrations will reduce dissolution rate. Consequently, ash leaching at Los Alamos involves the refluxing of the ashes in 10 M  $\text{HNO}_3$  - 0.3 M  $\text{CaF}_2$  for the first pass, 10 M  $\text{HNO}_3$  - 0.25 M  $\text{CaF}_2$  on the second pass, and 10 M  $\text{HNO}_3$

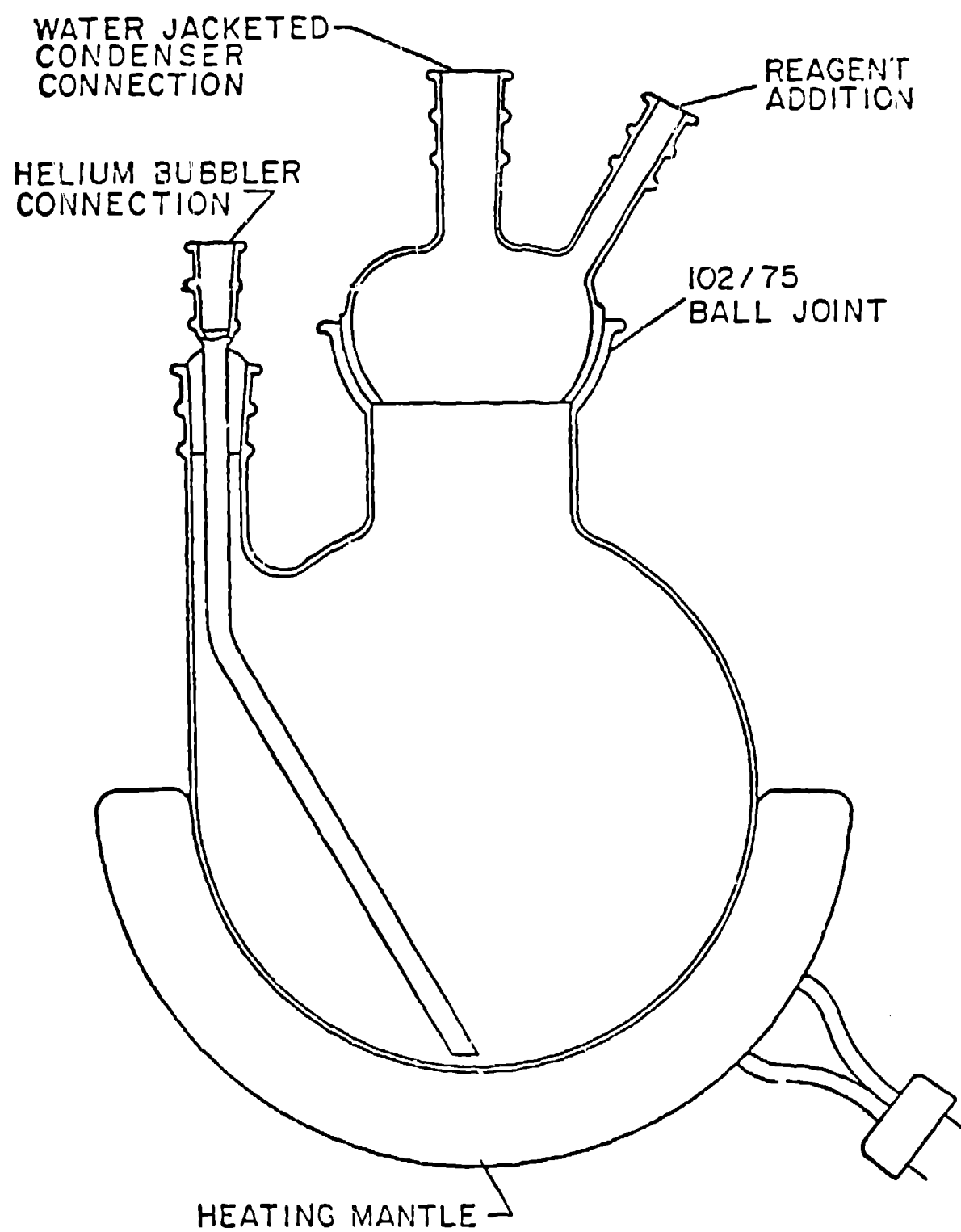


FIGURE 5 Five Liter Dissolution Vessel

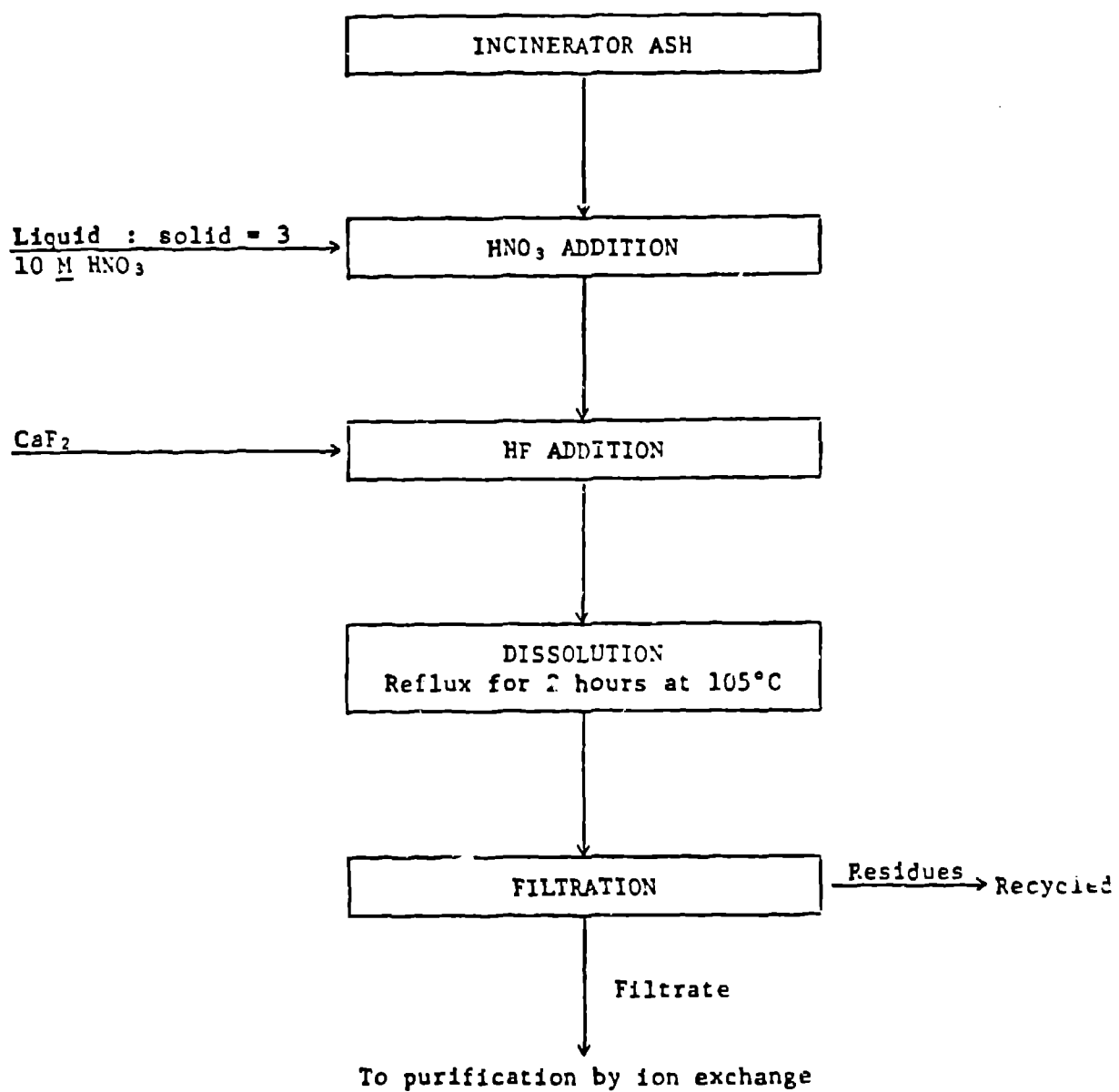


FIGURE 6 Dissolution of Incinerator Ash

on the third and subsequent passes. The volume of acid is determined by the vessel size and the need to have three volumes of acid per volume of ash. The solution is refluxed for two hours, filtered, and stored in 6 inch criticality-safe geometry tanks prior to transfer of the solutions to the ion exchange process. The residues are washed with dilute  $\text{HNO}_3$  and dried prior to NDA determination of the plutonium content in order to determine if the residues are to be discarded or recycled.

A detailed description of the chemical processing of the multitude of scrap residues generated in research and development programs is beyond the purview of this paper, but the interested reader is directed to an excellent review, LA-3542, published by Christensen and Maraman.

Since 1959, the Chemical Operations Section at Los Alamos has employed nitrate anion exchange as the primary method of scavenging, purifying, and concentrating plutonium. The general procedure for any residue is to get the plutonium into solution, as outlined above, sorb the plutonium on nitrate anion exchange resin, wash with sufficient 7  $\text{M}$   $\text{HNO}_3$  to remove impurities, elute the plutonium, precipitate the trivalent plutonium oxalate, and calcine the plutonium oxalate to the purified  $\text{PuO}_2$ .

The basic steps of the nitrate anion exchange procedure are to stabilize the plutonium in the tetravalent state, adjust the feed solution to the desired  $\text{HNO}_3$  concentration, sorb the plutonium on DOWEX 1 - X 4, 50 to 100 mesh, nitrate form resin, wash with the proper volume of 7  $\text{M}$   $\text{HNO}_3$ , and elute the purified plutonium with 0.3 - 0.48  $\text{M}$   $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ . The details of this procedure are shown in the flow diagram in Figure 7.

Plutonium in aqueous solutions can co-exist in four valence states, either in a single state or in nearly any combination of all four valences. This behavior is unique to plutonium and is due mainly to two factors:

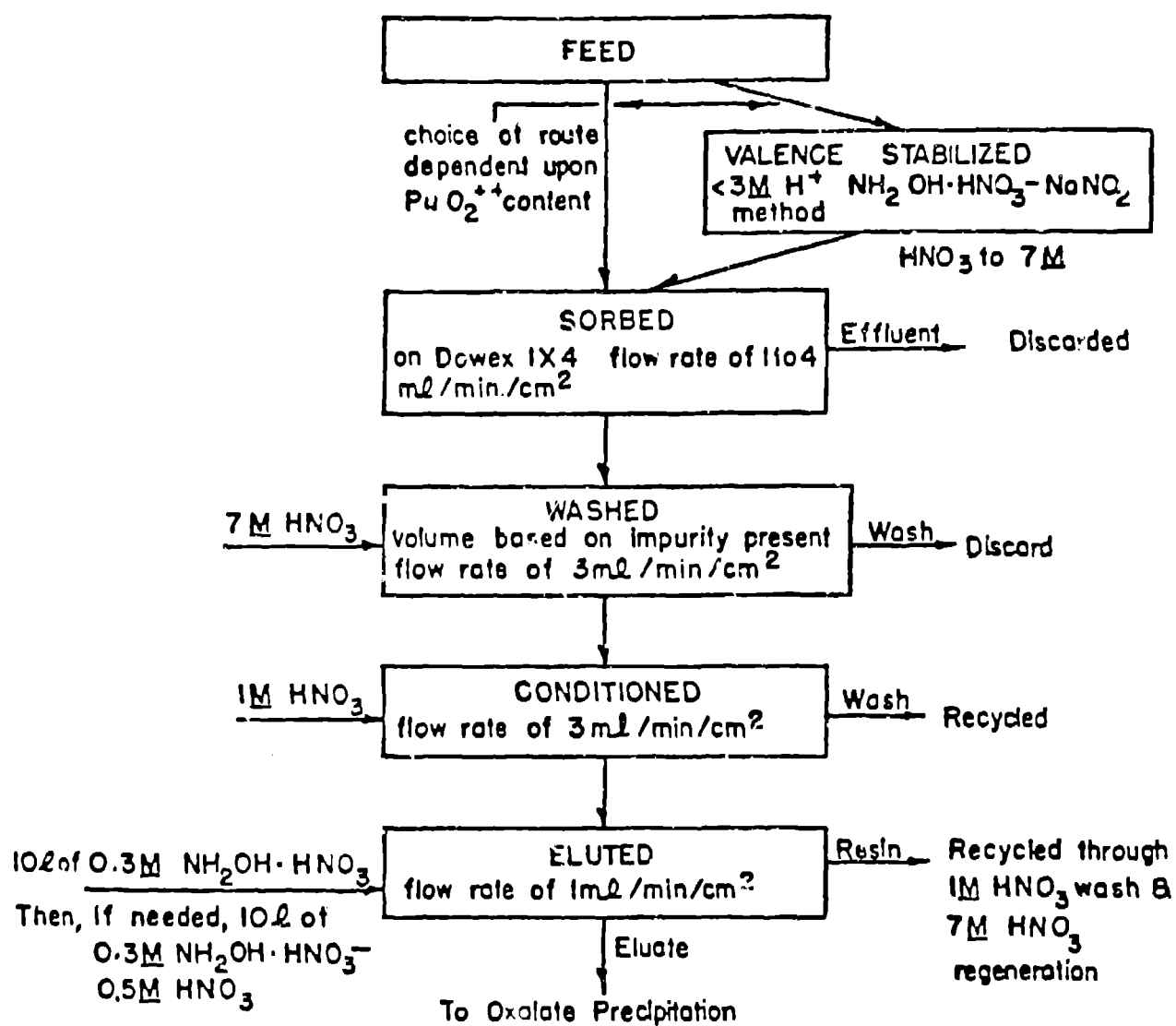
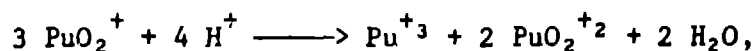
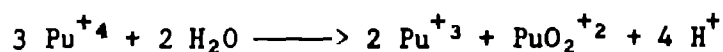


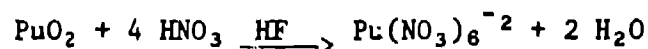
FIGURE 7 Nitrate Anion-Exchange Processing of Plutonium

1. the tendency of Pu(IV) and Pu(V) ions to disproportionate according to the following overall reactions:



2. the slow rate of reactions involving the formation or rupture of plutonium-oxygen bonds as compared to the much faster reactions involving only electron transfer.

Plutonium is also one of the very few elements which forms anion nitrate complexes which allows for the absorption of plutonium (IV) nitrate



out of nitrate solutions by anion exchange resins and offers a method for achieving a high degree of purification of plutonium. The preferred method is to stabilize the plutonium in the tetravalent state, the valence required for efficient sorption on the resin. The formation of the nitrate complex is dependent on the acid concentration of the feed solutions. For solutions less than 3 M HNO<sub>3</sub>, the following treatment is used (also see Figure 8): 9 liters of 2.2 M Al(NO<sub>3</sub>)<sub>3</sub> is added per 40 liters of feed to complex any fluoride present. This is followed by 300 ml of solution containing 300 g urea and 100 g Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>. Two liters of 1.9 M NH<sub>2</sub>OH·HNO<sub>3</sub> are then added, and the solution is allowed to digest for 4 - 8 hours. The Al(NO<sub>3</sub>)<sub>3</sub> maintains the required NO<sub>3</sub><sup>-</sup> concentration as well as complexing any fluoride ions. The urea is added to remove any nitrite that would consume a portion of the reducing agent before it could react with the plutonium. The strong reducing agent ferrous ammonium sulfate is added to quantitatively reduce the plutonium in case complexing agents such as oxalate or sulfate are present. The NH<sub>2</sub>OH·HNO<sub>3</sub> is also added to adjust the valence to the trivalent state. After the solution has digested for at least 4 hours, the plutonium

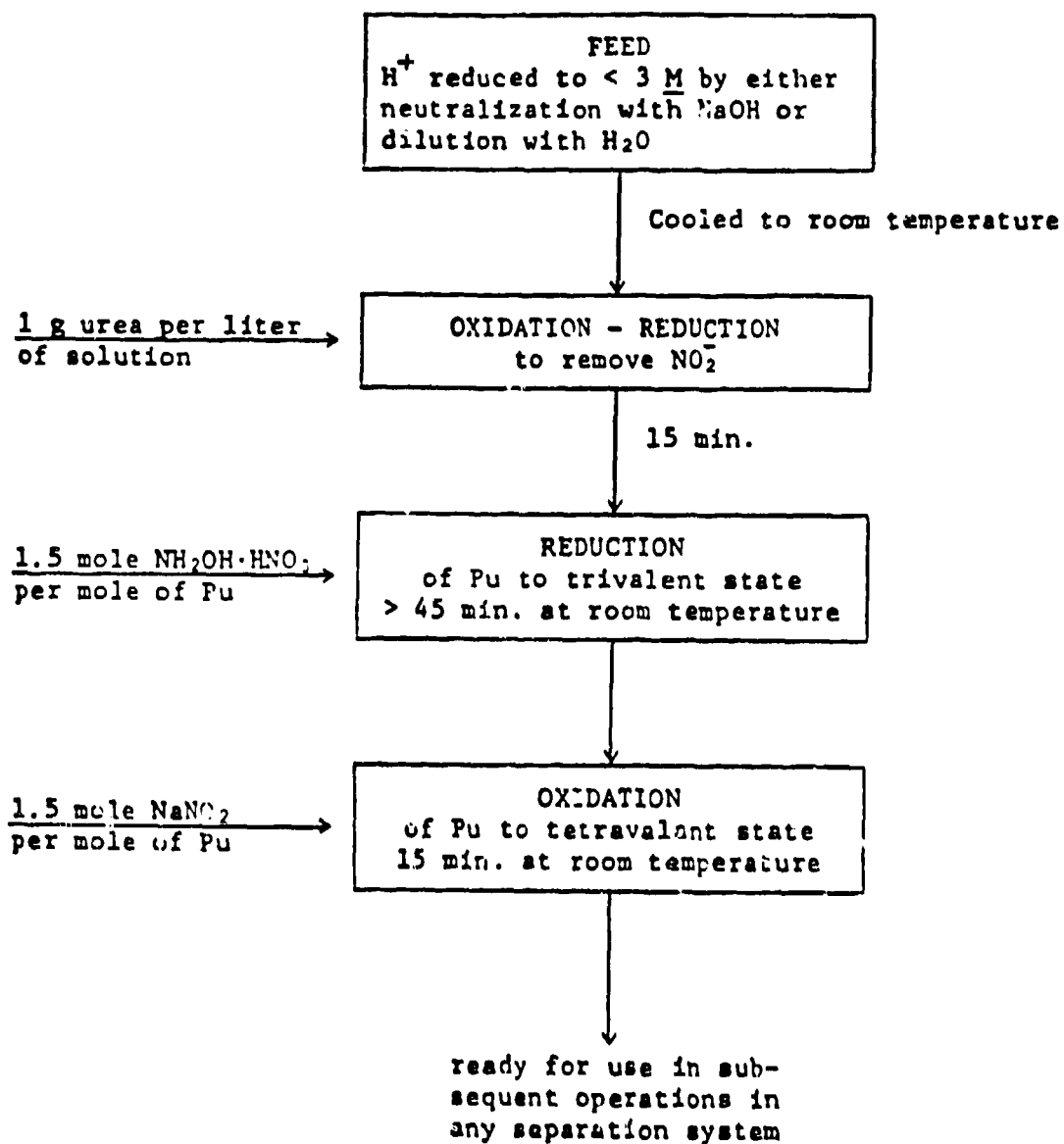


FIGURE 8 Stabilization of Tetravalent Plutonium

has been converted to the trivalent state. Upon addition of  $\text{NaNO}_2$ , the Pu is oxidized to the tetravalent state via the following reaction:



For solutions greater than 3 M  $\text{HNO}_3$ , a less rigorous treatment is employed consisting of 300 g  $\text{NaNO}_2$  and 500 ml of 2.2 M  $\text{Al}(\text{NO}_3)_3$ .

After the 7 M  $\text{HNO}_3$  feed solution has been pumped through the 6 inch column and the plutonium has been sorbed on the resin, the resin bed is washed with 7 M  $\text{HNO}_3$  to remove impurities.

The distribution coefficients of several elements have been measured from 7 M  $\text{HNO}_3$  at 25°C on DOWEX 1 - X4. Based on these data, the probable impurities can be divided into three groups (Figure 9) according to the degree of sorption on the resin:

1. elements that are apparently not sorbed, distribution coefficient = 0,
2. elements that are weakly sorbed, distribution coefficient = 0 - 4,
3. elements that are strongly sorbed, distribution coefficient > 4.

Routinely, one or two column volumes (where volume refers to void volume) of wash are sufficient to remove from the column impurities that are not sorbed by the resin. Removal of the weakly sorbed impurities is more complex due to a "kinetic trapping" mechanism in which the sorbed plutonium impedes the washing of the impurities from the resin bed. In many instances, this effect necessitates a much greater volume of wash than would be expected from a simple, no interaction model using the distribution coefficients as a guide. For example, zirconium, with a distribution coefficient of 0.38, should be easily removed by 3 or 4 column volumes of wash (15 - 20 liters of 7 M  $\text{HNO}_3$ ), yet experience has shown that 6 - 8 column volumes (30 - 40 liters) are required before the zirconium content of the eluate will be reduced to < 50 ppm based on plutonium.



ELEMENTS		
NO SORPTION Distribution Coefficient = 0	WEAK SORPTION Distribution Coefficient < 4	STRONG SORPTION Distribution Coefficient > 4
Mg	Sc	Pd
Al	As	Ir
Ti	Sa	Pt
V	Zr	Au
Cr	Nb	Th
Mn	Mo	
Fe	Ru	
Co	Ag	
Ni	Cd	
Cu	La	
Zn	Hf	
Ga	W	
Ge	Re	
Y	Os	
In	Hg	
Sn	Pb	
Sb	Bi	
Ta	Ce	
Tl	Rare Earths	
	U	
	Am	
	Rh	

FIGURE 9 Classification of Elements by Degree of Sorption

DOWEX 1 - X4 Resin from a Nitrate Media

Uranium, with a distribution coefficient of 3.9, in ratios up to 6 to 1 with plutonium, routinely requires 40 column volumes (200 liters) of wash to lower the uranium content to  $< 100$  ppm in the purified  $\text{PuO}_2$ .

The elements having a distribution coefficient greater than 5 cannot be effectively processed by anion exchange without either poisoning the resin bed or following the plutonium through the purification process.

Following the washing of impurities from the resin bed, the plutonium must be converted to the trivalent state to facilitate the stripping of the column. The plutonium is reduced from the tetravalent to the trivalent form by the addition of hydroxylamine nitrate ( $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ ). The elution process consists of first reverse flushing the column with 10 liters of 1  $\text{M}$   $\text{HNO}_3$ , thus insuring that there will not be a violent reaction between the hydroxylamine nitrate and concentrated ( $> 3 \text{ M}$ ) nitric acid. The plutonium is eluted from the column with 10 liters of 0.3 - 0.48  $\text{M}$   $\text{NH}_2\text{OH}\cdot\text{HNO}_3$  and then 15 liters of 0.3 - 0.48  $\text{M}$   $\text{NH}_2\text{OH}\cdot\text{HNO}_3$  - 0.5  $\text{M}$   $\text{HNO}_3$ . No more than 10 liters of  $\text{NH}_2\text{OH}\cdot\text{HNO}_3$  are passed through the column without the addition of 0.5  $\text{M}$   $\text{HNO}_3$  to insure that the acidity in the column is maintained at  $> 0.5 \text{ M}$  to prevent the irreversible formation of insoluble polymeric plutonium.

The deep blue eluate is now ready for the oxalate precipitation step. This step accomplishes two basic goals:

1. the plutonium is converted from the nitrate form into a solid form that is easily converted to  $\text{PuO}_2$
2. a partial decontamination is provided from impurities such as Fe, Al, and U.

The feed solution for this step is approximately 0.5 - 1  $\text{M}$   $\text{H}_2\text{O}_2$  and 0.4  $\text{M}$   $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ . Consequently, all of the Pu is in the trivalent state, and the precipitation of trivalent plutonium oxalate can be affected with no addi-

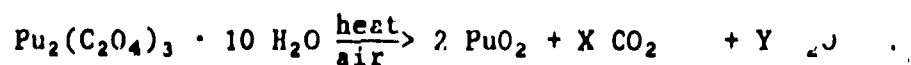
tional treatment. The precipitation is performed on 5 liter aliquots containing 100 - 140 g Pu by the addition of 275 g of oxalic acid crystals. The precipitation of trivalent plutonium oxalate according to the reaction:



is preferred over the tetravalent precipitation for several reasons:

1. less control of precipitation conditions is required
2. the resulting precipitate settles and filters more rapidly
3. decontamination from impurities is good
4. filtrate losses are low.

The blue-green  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O}$  is collected by filtration, washed with several 0.5 M  $\text{HNO}_3$  portions, and dried by applying suction to the filter cake. Figure 10 shows the general flow diagram for the oxalate precipitation. The oxalate filter cake is then transferred to a stainless steel furnace beaker and heated in a furnace for six hours at 450 - 500°C with occasional stirring. This converts the plutonium oxalate to the yellowish-green  $\text{PuO}_2$  according to the reaction:



The  $\text{PuO}_2$  is transferred to a stainless steel container and a plutonium value is determined. The  $\text{PuO}_2$  is then double canned for storage as the final product form. Figure 11 shows the results from an analysis of the purified  $\text{PuO}_2$  after anion exchange, oxalate precipitation, and calcination to the oxide form. Plutonium dioxide is the most important compound of plutonium due to its high melting point, approximately 2400°C, its chemical stability, and radiation stability.

Solutions are treated in 6 inch diameter glass tanks and stored in 6 inch diameter stainless steel tanks equipped with see-through glass pads on

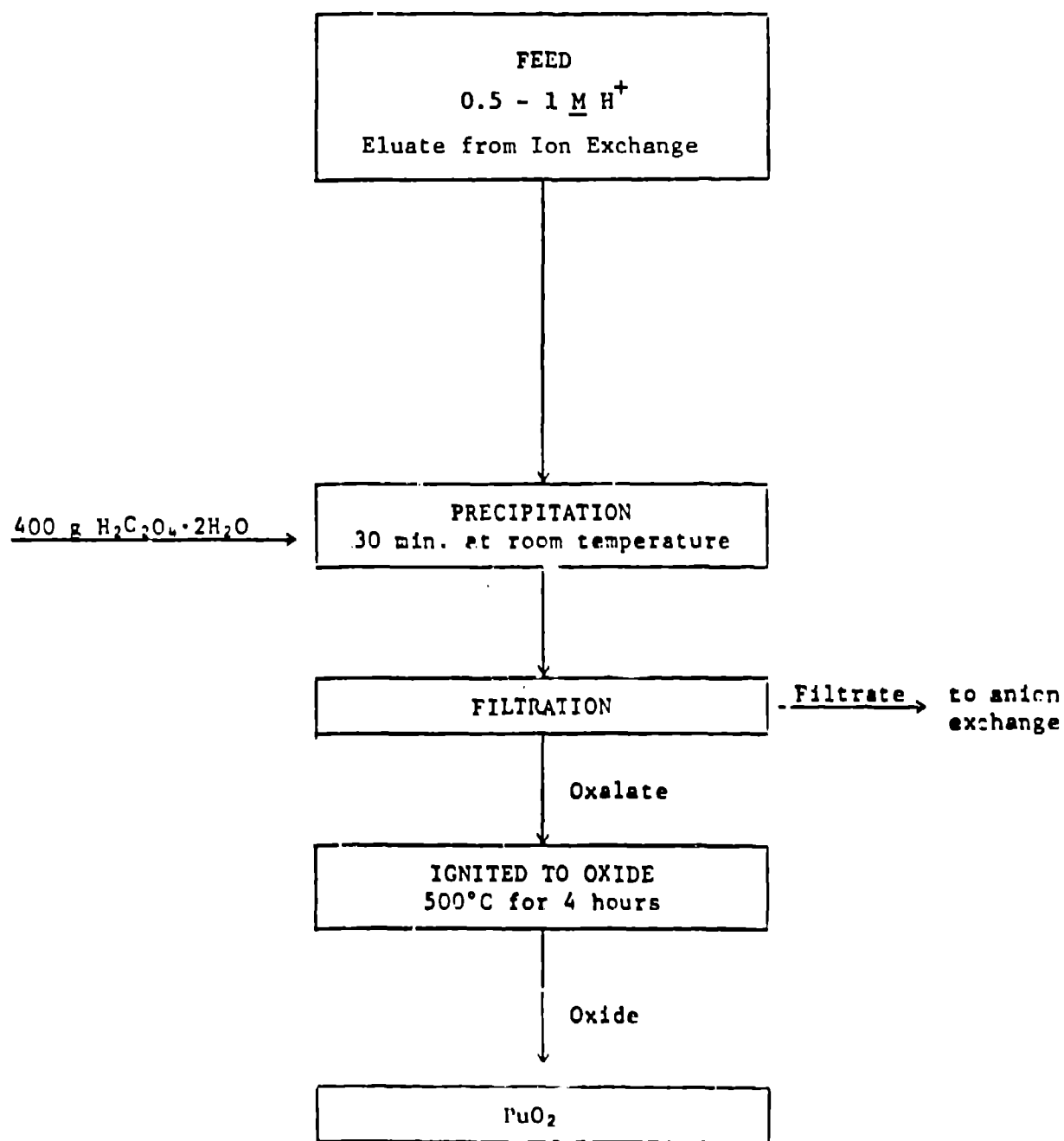


FIGURE 10 Plutonium Oxalate Precipitation

<u>Impurity</u>	<u>Concentration, (ppm by weight)</u>
Lithium	< 1
Beryllium	< 1
Boron	50
Sodium	60
Magnesium	1
Aluminum	25
Silicon	500
Potassium	60
Calcium	300
Vanadium	< 3
Chromium	20
Iron	90
Cobalt	< 3
Nickel	10
Copper	2
Zinc	< 5
Zirconium	< 100
Molybdenum	< 3
Cadmium	< 10
Samarium	< 5
Europium	< 5
Gadolinium	< 5
Dysprosium	< 5
Tantalum	< 100
Tungsten	< 10
Lead	25

FIGURE 11 Analytical Data for  $\text{PuO}_2$  Purified  
by Nitrate Anion Exchange and Oxalate Precipitation

either end of the horizontal tanks and on the sides of the vertical tanks (Figure 12, CN78-8866). These tanks are geometrically favorable to > 500 g plutonium per liter. The movement of plutonium is documented by the use of computer terminals located in each process area. The item identification, location, volume or bulk weight, plutonium content, and the type of material is recorded for each batch of plutonium in the facility.

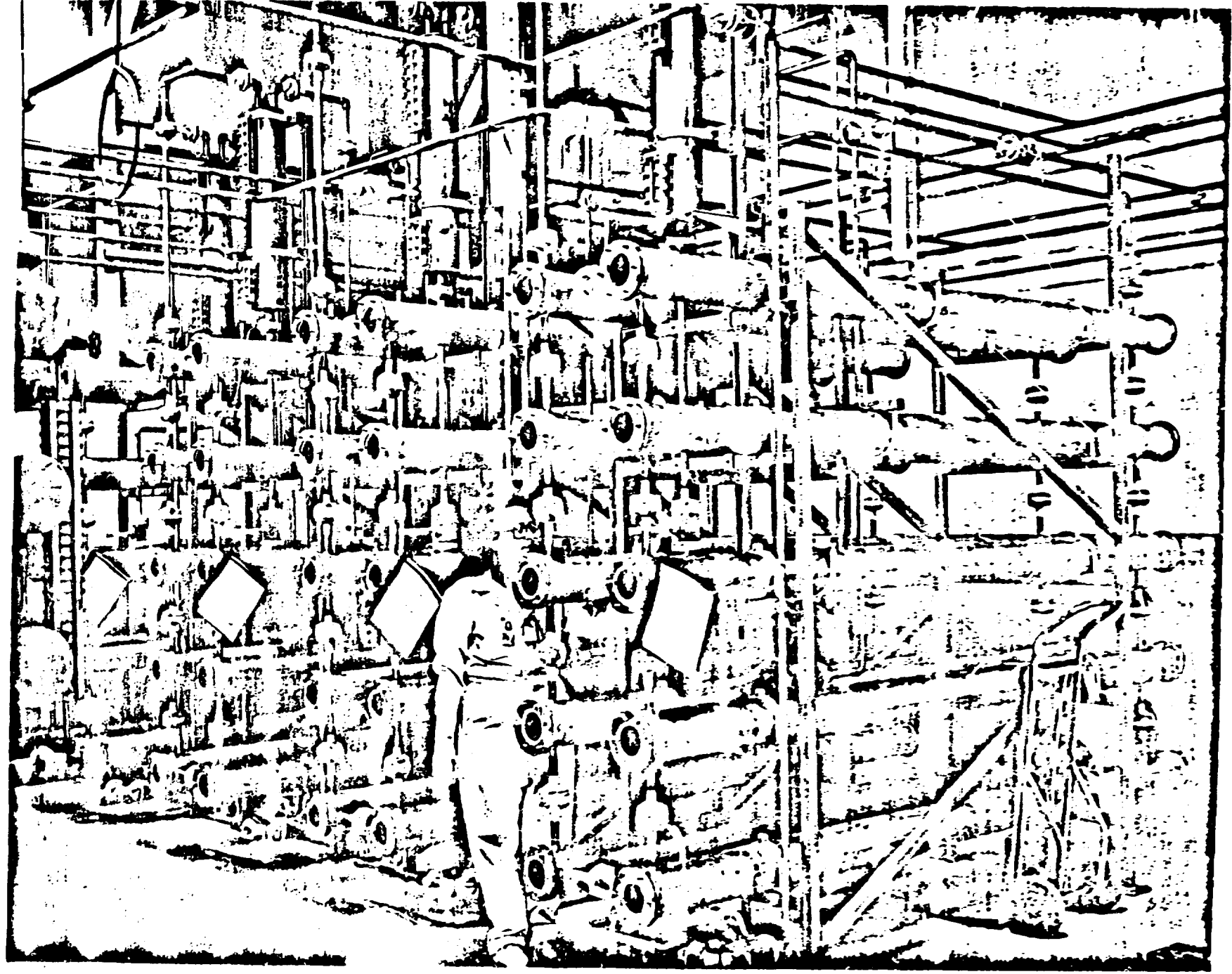


FIGURE 12      Vertical Tanks

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